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^{1}H- AND ^{13}C-NMR SPECTRA OF SOME AZOMETHINES OF 5-AMINO-2-PHENYLINDOLE SERIES

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SUMMARY

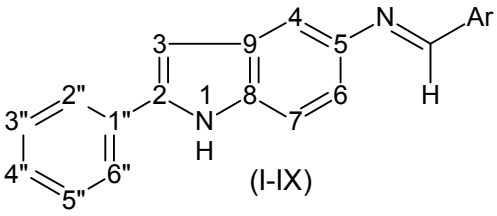
The ^{1}H- and ^{13}C-spectra of some azomethines of 5-amino-2-phenylindole series have been recorded and researched. It shown that, the substituents in benzene ring influenced on the chemical shift of proton on azomethine bond.

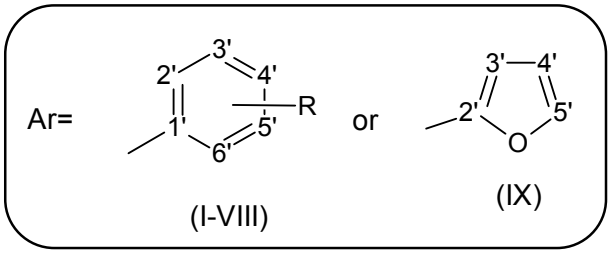
I - INTRODUCTION

Some azomethines of 5-amino-2-phenylindole have been synthesized from this amine and some different substituted benzaldehydes in our lab [1]. Their properties, as the metallic corrosion inhibition capacity on CT-3 steel in 2 M HCl medium, were investigated [2]. In some previous papers, we indicated that the azomethines containing indole ring had some interesting spectral properties [3 - 5]. In order to continuing these studies, the proton and carbon-13 NMR spectroscopies of these azomethine series have been recorded and discussed.

II - EXPERIMENTAL

Azomethines of 5-amino-2-phenylindole series what were used in this research have been synthesized in according to the method described [1]. Their structures have the following formulas:





where, R were m-NO_2(I); p-Cl(II); H(III); 3',4'-O_2CH_2(IV); p-OCH_3(V); p-OH(VI); p-$N(CH_3)_2$(VII); o-OH(VIII).

The ^{1}H and ^{13}C-NMR spectra were recorded in AVANCE Spectrometer (BRUKER, German) at 500 MHz, using DMSO-d_6 as solvent, using TMS as the internal reference.

III - RESULTS AND DISCUSSION

All signals in ^{1}H-NMR spectra of benzylidene-5-amino-2-phenylindoles were represented in table 1. It shown that total of protons in the azomethine molecules was suitable to molecular formulas. The sharp resonance signal with high intensity that appears in region

of 11.500 ppm to 11.683 ppm belongs to NH-proton in the indole ring. This signal can be easily distinguished from other ones (see figure 1). The resonance signal of proton in azomethine bond (>CH=N–) is the singlet peak and has medium intensity. This signal appears in region of 8.496 ppm to 9.028 ppm. Both these signals NH and >CH=N– are always in the low field.

Table 1: Chemical Shifts in ^{1}H-NMR spectra of azomethines of 5-amino-2-phenylindole series (in DMSO)

Substituents	Chemical Shifts, δ (ppm) (J, Hz)								
	m-NO_2	*p*-Cl	H	3',4'-O_2CH_2	*p*-OCH_3	*p*-OH	*p*-$N(CH_3)_2$	o-OH	furfuryl
Protons (multip.)	(I)	(II)	(III)	(IV)	(V)	(VI)	(VII)	(VIII)	(IX)
N-H (s)	11.652	11.608	11.590	11.558	11.549	11.528	11.500	11.683	11.583
H3	6.955(s)	6.931 (br)	6.934(d) J =1	6.913 (br)	6.913 (br)	6.901 (br)	6.889(d) J=1	6.959 (br)	6.921(d) J=1
H4	7.588(s)	7.510 (br)	7.509(d) J=2	7.507 (br)	7.433 (br)	7.396(s)	7.372(d) J = 1.5	7.631 (br)	7.906 (br)
H6 (dd)	7.266 J_1=9 J_2=1.5	7.199 J_1=8.5 J_2=1	7.189 J_1=8.5 J_2=1.5	7.136 J_1=8.5 J_2=1.5	7.136 J_1=8.5 J_2=2	7.106 J_1=8.5 J_2=1.5	7.090 J_1=8.5 J_2=2	7.281 J_1=8.5 J_2=1.5	7.141 J_1=8.5 J_2=1.5
H7 (d)	7.463 J=9	7.439 J=9	7.439 J=8.5	7.405÷ 7.435	7.415 J=8.5	7.404 J=7.5	7.391 J=8.5	7.477 J=8.5	7.415 J=8.5
$H_{azomethine}$ (s)	8.755	8.737	8.726	8.600	8.624	8.552	8.496	9.028	8.529
H2'	8.917 (s)	7.966(d) J=8.5	7.955 (dd) J_1 = 7.5; J_2=2	7.405÷ 7.435	7.894 (d) (J=8.5)	7.783(d) J=8.5	7.754(d) J=8.5	–	–
H6'	8.328 (dd) J_1= 8.5; J_2= 1.5	7.966(d) J =8.5	7.955 (dd) J_1=7.5 J_2=2	7.405÷ 7.435	7.894 (d) J=8.5	7.783(d) J=8.5	7.754(d) J=8.5	7,639 (d) J=7.5	–
H3'	–	7.575(d) J=8	7.511(t) J=5.5	–	7.067 (d) J=8.5	6.887(d) J=9	6.788(d) J=9	6.967(d) J=6.5	7.089(d) J=3.5
H5'	7.806(t) J=8	7.575(d) J=8	7.511(t) J=5.5	7.048 (d) J= ??.5	7.067 (d) J= 8.5	6.887(d) J=9	6.788(d) J=9	6.972(t) J=??	7.458 J=7
H4'	8.370(d) J= 7.5	–	7.507(t) J=6	–	–	–	–	7.382 J=7.5	6.694 (dd) J_1 = 3.5; J_2 =2
H2", H6" (d)	7.869 J=7.5	7.871 J=7.5	7.874 J=7.5	7.864 J=7.5	7.866 J=7.5	7.862 J=7.5	7.860 J=7.5	7.881 J=7.5	7.865 J=7.5
H3", H5" (t)	7.472 J=7.5	7.468 J=8	7.471 J=7.5	7.465 J=7.5	7.466 J=7.5	7.463 J=7.5	7.461 J=7.5	7.476 J=7.5	7.465 J=7.5
H4" (t)	7.333 J=7.5	7.326 J=7.5	7.327 J=7.5	7.321 J=7.5	7.321 J=7.5	7.317 J=7.5	7.315 J=7.5	7.337 J=7.5	7.324 J=7.5
Other H				CH_2: 6.117(s)	CH_3: 3.836(s)	OH: 9.987(s)	CH_3: 3.002(s)	OH: 13.674(s)	

(s: singlet; br: broad; d: doublet; dd: double doublet and t: triplet).

The chemical shifts of proton in the substituted benzene nucleus in the position 2 of indole ring (H2", H3", H4", H5" and H6") are trivially affected by the present of different substituents. For example, protons H2" and H6" have doublet signals in the narrow region from 7.860 to 7.881 ppm; protons H3" and H5" have triplet signals with chemical shift δ_H = 7,461 ÷ 7,476 ppm; and the resonance signal of proton H4" is a triplet one in region from 7.315 to 7.337 ppm. It shown that, the resonance signal of proton H3 is easily recognized as a singlet one in the high field at 6.889 ÷ 6.959 ppm. Protons H6 have double doublet signals and H7 have doublet signals, with δ(H6) < δ(H7), in region of 7.090 ÷ 7.477 ppm; sometimes, these signals overlap each other and raise difficulties in distinguishing them.

We recognized that there is an order of chemical shifts of substituted benzylidene-5-amino-2-phenylindoles (I-VIII) as following: *p*-$N(CH_3)_2$<*p*-OH<*p*-OCH_3<3',4'-O_2CH_2<H<*p*-Cl<*m*-NO_2. The linear regression between chemical shift δ_H and Hammett's σ constants in azomethines of 5-amino-2-phenylindole series is represented in figure 2.

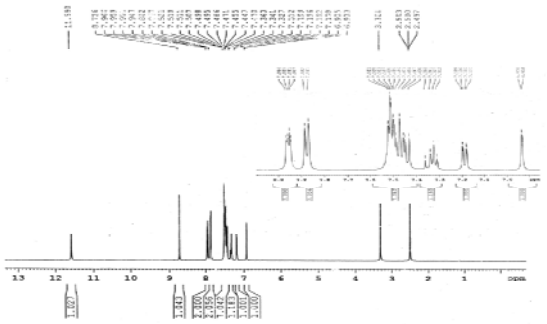
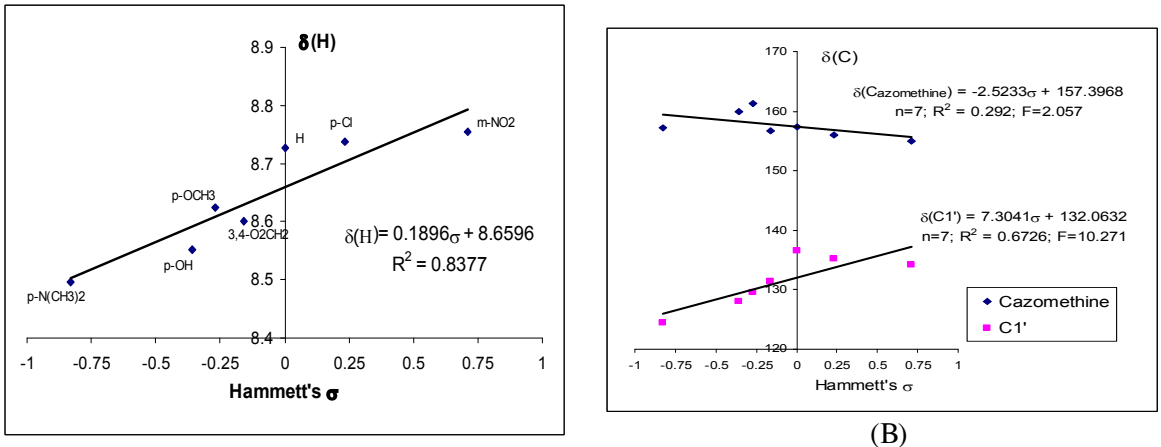


Figure 1: ^{1}H-NMR spectrum of benzylidene-5-amino-2-phenylindole

This regression can be expressed by following equation: $\delta_X = 0.1896\sigma + 8.6596$ (n = 7, $R^2 = 0.8377$, F = 25.81).

This equation with the slope α = 0.1896 > 0 indicated that the electron-donating substituents (with σ < 0) cause the upfield shift of $\delta_{Hazomethine}$ and the electron-withdrawing substituents (with σ > 0) cause the downfield shift of this chemical shift values. However, this influences are insignificant which are expressed the small value of α, so it could indicated the dependence of chemical shift of these carbon atoms on their density charge.



(A) (B)

Figure 2: Linear correlation regression between chemical shift δ_H (A) and δ_C (B) with the Hammett's σ constants in azomethines of 5-amino-2-phenylindole series

The ^{13}C-NMR spectra of these azomethines have been recorded. The chemical shifts on carbon atoms in these azomethines are represented in table 2.

From table 2, it has indicated that the resonance signal of carbon atom on the azomethine bond was always in the low field at 152.460 ÷ 161.382 ppm. This signal can be

distinguished from another one of other carbon atoms. In case of the benzene nucleus in position 2 of indole ring, the resonance signals of pairs of carbon atoms C2" and C6", C3" and C5" have the more intensive ones and are in regions of 124.894 ÷ 125.044 ppm and 128.686÷128.898 ppm, respectively. The carbon atoms C1" and C4", in turn, have the resonance signals in regions of 130.360 ÷ 132.150 ppm and 127.408 ÷ 127.624 ppm, respectively.

Table 2: Chemical Shifts in ^{13}C-NMR spectra of azomethines of 5-amino-2-phenylindole series (in DMSO)

Substituents	Chemical Shifts, δ (ppm)								
	m-NO_2	*p*-Cl	H	3,4-O_2CH_2	*p*-OCH_3	*p*-OH	*p*-$N(CH_3)_2$	*o*-OH	furfuryl
Carbon Atom	(I)	(II)	(III)	(IV)	(V)	(VI)	(VII)	(VIII)	(IX)
C2	138.844	138.700	138.608	138.549	138.496	138.439	138.320	139.042	138.645
C3	99.288	99.194	99.144	99.100	99.073	99.039	98.987	99.250	99.168
C4	112.538	112.010	111.739	111.606	111.585	111.562	111.509	112.308	111.774
C5	142.820	143.422	143.800	143.877	144.213	144.458	144.878	140.223	143.529
C6	116.519	116.478	116.473	116.511	116.493	116.500	116.575	116.074	116.268
C7	111.755	111.677	111.628	111.532	111.376	111.19	110.943	111.961	111.691
C8	136.522	135.455	136.108	135.950	135.864	135.752	135.556	136.480	136.146
C9	129.083	129.097	129.097	129.121	129.128	129.138	129.178	129.153	129.115
$C_{azomethine}$	155.024	155.944	157.321	156.617	161.382	160.014	157.171	160.397	152.460
C1'	134.212	135.235	136.569	131.444	129.505	128.065	124.504	118.898	115.284
C2'	122.190	128.829	128.238	106.053	129.946	130.144	129.748	160.238	145.616
C6'	138.224	128.829	128.238	147.924	129.946	130.144	129.748	132.193	–
C3'	148.227	129.822	128.858	149.613	114.163	115.545	111.509	116.436	–
C5'	131.937	129.822	128.858	101.547	114.163	115.545	111.509	119.533	112.302
C4'	124.871	136.252	130.719	108.335	156.781	157.066	151.962	132.413	145.355
C1"	130.360	131.944	132.023	132.063	132.079	132.108	132.150	131.873	132.006
C2", C6"	125.004	124.974	124.950	124.950	124.933	124.952	124.894	125.044	124.952
C3", C5"	128.884	128.876	128.686	128.874	128.865	128.867	128.852	128.898	128.875
C4"	127.557	127.504	127.456	127.45	127.425	127.408	127.353	127.624	127.482
Other carbon				δ_{CH2}: 39.596	δ_{CH3}: 55.314		δ_{CH3}: 39.722		

In case of substituted benzene nucleus of aldehyde component, the situation can be divided into two different groups. For *para*-substituted benzene nucleus (II-III and V-VII), the pair of carbon atoms C2' and C6' give the more intensive signals in region 128.238 ÷ 130.144 ppm, and carbon atoms C3' and C5' have similar ones in regions of 111.509 ÷ 129,822 ppm. The electron-donating substituents in *para*-position, such as OCH_3 (V), OH (VI), $N(CH_3)_2$ (VII), cause the chemical shifts of C3' and C5' to move upfield (with δ = 111.509 ÷ 115.545 ppm), while the electron-withdrawing substituents have some influences on the contrary.

The resonance signals in 13C-NMR spectra of carbon atoms in indole ring, essentially, were influenced by the present of the substituents in aldehyde component. The carbon atom C3 has lowest chemical shift, with δ_C = 98.987 ÷ 99.288

ppm and the carbon atom C5 has highest one, with δ_C=140.223÷144.878 ppm. The change regions of chemical shifts of different carbon atoms in azomethines I-VIII can be summarized as following from the high field signal to low field one (see table 3).

Similarly in case ^{1}H-NMR spectra, there were some linear correlation regression of carbon-13 chemical shifts of carbon atoms in position C1' and azomethine-carbon atom with Hammett's σ constants of substituents in benzene-aldehyde component. These relationships can be expressed by equations $\delta_{Cazomethine}$ = -2.5233σ + 157.3968 (n = 7; R^2 = 0.292; F = 2.057) and $\delta_{C1'}$ = 7.3041σ + 132.0632 (n = 7; R^2 = 0.6726; F = 10.271), respectively. The slopes of those equations are opposite signs ($\alpha_{Cazomethine} < 0$ and $\alpha_{C1'} > 0$), it is indicated that the substituents on benzene-aldehyde ring have opposite influences on the position of carbon-13 chemical shift of these carbon type: The electron-donating substituents (σ < 0) make $\delta_{Cazomethine}$ moving to downfield and $\delta_{C1'}$ moving to upfield, and on the contrary, the electron-withdrawing substituents (σ > 0) cause $\delta_{Cazomethine}$ to appear upfield and $\delta_{C1'}$–downfield.

Table 3: Region of chemical shifts in ^{13}C-NMR spectra of azomethines of 5-amino-2-phenylindole series (in DMSO)

Carbon	Region (δ, ppm)	Carbon	Region (δ, ppm)	Carbon	Region (δ, ppm)
C2	138.320 ÷ 139.042	C8	135.455 ÷ 136.522	C1'	118.898 ÷ 136.569
C3	98.987 ÷ 99.288	C9	129.083 ÷ 129.138	C2'	122.190 ÷ 160.238
C4	111.509 ÷ 112.538	C1"	130.360 ÷ 132.150	C3'	111.509 ÷ 149.613
C5	140.223 ÷ 144.878	C2" C6"	124.894 ÷ 125.044	C4'	108.225 ÷ 157.066
C6	116.074 ÷ 116.575	C3" C5"	128.686 ÷ 128.898	C5'	101.547 ÷ 131.937
C7	110.943 ÷ 111.76	C4"	127.408 ÷ 127.624	C6'	128.238 ÷ 147.924
		$C_{azomethine}$	155.024 ÷ 168.382		

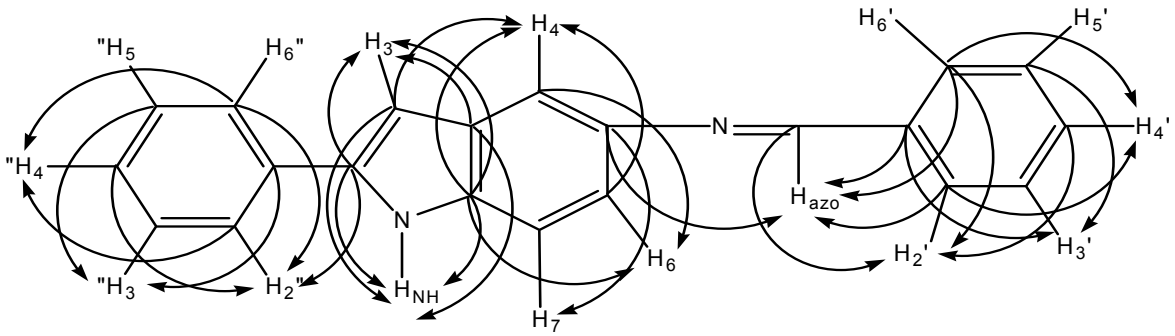


Figure 3: The C-H interactions in HMBC spectrum of benzylidene-5-amino-2-phenylindole

The long and short C–H interactions can be shown in the NMR spectra with two-dimensional experiment, HSQC and HMBC respectively. In the HSQC spectrum of azomethine III (R=H), it's indicated that the short-range C–H interactions in each C–H bond, as following pairs: C3–H3; $C_{azomethine}$–$H_{azomethine}$, C4–H4, C2" and C6" with H2" and H6"; C4"–H4"; C2' and C6' with H2' and H6'. The HMBC spectrum of azomethine III (R=H) that is represented in figures 3 and 4 indicated some long-range C–H interactions in azomethine molecules.

IV - CONCLUSIONS

The ^{1}H- and ^{13}C-spectra of some azomethines of 5-amino-2-phenylindole series have been recorded and researched. It shown that, the substituents in benzene ring influenced

on the chemical shift of proton on azomethine bond.

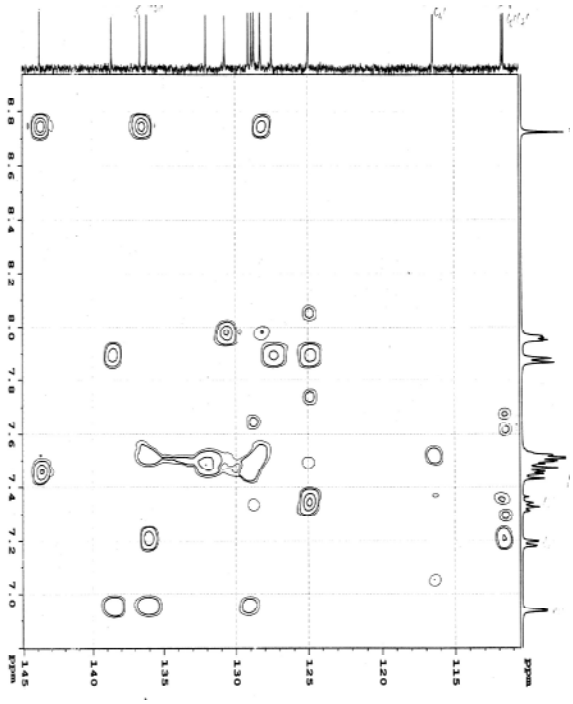


Figure 4: A part of HMBC spectrum of benzylidene-5-amino-2-phenylindole

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